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SPECIFICATION OF EQUIPMENT AND METHODOLOGY FOR THE AUTOMATED CONDUCTIVITY TESTING OF CERAMICS

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Introduction

The understanding of the electrical properties of solids and solid-liquid interfaces is of fundamental importance in the design of energy storage devices such as solar cells and fuel cells. A method for the measurement of these properties is known as the a.c. impedance technique which involves the perturbation of the system by a small amplitude, a.c. voltage. Although this technique has been used widely to measure the properties of electrode interfaces, it has recently become popular for the measurement of the ionic conductivity of solids.

Historically impedance spectra have been determined by the use of a.c. bridges (Figure 7). Such bridge methods whilst being capable of high accuracy can be extremely time consuming and laborious as the determination of a complete impedance spectrum with e.g. 20 points per decade of frequency could take several hours. This led to the demand for more rapid methods of determining the impedance. Early improvements for the impedance measurement employed phase sensitive detectors and gain phase meters. In contrast to indirect methods involving the Fourier transform of perturbing waveforms such as aperiodic transients and pseudo-random white noise, this direct approach has the advantage of being relatively straight-forward. The most serious criticism of this method is that measurements must be performed at each frequency in a serial fashion. This objection has been largely overcome by automation using the new generations of minicomputers and a number of systems have been reported.

It is the purpose of this report to describe the essential requirements of such a system as required for the measurement of the ionic conductivity of solids. Thus both the computing facilities and the measurement

instruments will be discussed in detail and where possible, recommendations as to particular instruments will be given.

Minicomputer/calculator and peripherals

The choice of calculator must be made on the basis of software and interfacing capabilities. Although storage capacity is important, most calculators on the market have add-on memory capabilities making this less critical.

a) Software

BASIC is the almost universal language of the scientific calculators on the market today (a notable exception is the Hewlett Packard 9825 calculator which uses HPL. This is an excellent and highly sophisticated language but which requires a high degree of programming expertise and cannot therefore be recommended in connection with the present system). However the exact form of BASIC varies from manufacturer to manufacturer and sometimes from model to model. Thus it is not usually possible to run a programme developed on one calculator on one from a different manufacturer and calculators can therefore not be interchanged. Updating of calculators and fundamental changes in the BASIC used can often make a calculator obsolete within a few years. This is especially true of the cheaper calculators. Howlett Packard have a good name in this area and it is unlikely that any of their calculators will become obsolete in the foreseeable future.

A desirable feature of a calculator is the possibility to programme a priority interrupt. This allows the operator to interact with the calculator even when the calculator is controlling measurement. This becomes particularly important when long term experiments such as the measurement of the temperature dependence of the ionic conductivity are envisaged.

Similarly programming errors and breakdown of the measurement equipment should not result in an irretrievable loss of data which has possibly been collected over a considerable length of time. Neither of these features are available on the cheaper calculators.

An almost standard option of modern calculators is a visual display unit (VDU) and this is a highly desirable feature allowing the continuous monitoring of an experiment. As monitoring is best performed graphically, it is desirable that graphs can be plotted on the VDU (VDUs can have alphanumeric, semi-graphic or full graphic display). Speed of operation including programme loading and data storage is also an important feature. With the cheaper calculators, this can only be achieved by the purchase of a flexible disc drive.

b) Interfaces

It is possible to build interfaces to interconnect most equipment in laboratories where high technical ability and electronics expertise is available, this can be a convenient method of interfacing a computer to a wide range of instruments. However this expertise is not readily available in the majority of laboratories and the interfacing flexibility is therefore reduced. The most versatile and readily available type of interface is the IEEE-488 (HP-IB) bus and this must be a highly recommended option in the choice of the calculator and all peripheral equipment. This requirement, however, rules out the choice of some of the cheaper calculators such as Apple which does not have this possibility. However other types of interfacing are possible and it is highly desirable that the purchased calculator has as many interfacing options as possible.

c) Storage Capacity

The storage capacity of calculators is measured in kilobytes (1000 bytes), being typically incremented in 8k blocks. A typical control programme and interfacing requires approximately 16k bytes of memory and it is thus essential that the calculator has at least 32k bytes of memory to give sufficient flexibility without the purchase of auxiliary equipment.

On the basis of the above requirements, it is possible to suggest a number of different systems and these are listed in Table 1 together with their operating characteristics. For convenience, the approximate costs of the suggested packages are also included although no guarantee to their accuracy is given. It can be seen that the PET calculator when purchased with a flexible drive and tractor printer would meet the essential requirements discussed above. However the software has been changed 3 times in the past two years and does not allow priority interrupts or error control. Adequate speed of operation is only achieved by purchase of a flexible drive. (Note: the cassette drive which is included in the price is not controllable by the calculator and does not therefore represent a good data storage medium.) The Hewlett Packard System 35 meets most of the desirable features listed above although the optional VDU has not graphics programming and all interfacing is optional (at extra cost). The system 45T is the only calculator which meets all of the essential and desirable requirements discussed above.

A final point which is worthy of discussion is that the basic system described here relies on the calculator being totally dedicated to measurement, perhaps being totally tied up for up to 24 hours. This is a non-trivial point especially when one considers the range of possibilities

TABLE 1

Features of Calculator and Peripherals Meeting Essential Requirements

	Pet 4032 Pet Flexible Drive Pet Tractor Printer	HP 9800 System 35 Printer	HP 9800 System 45T
a) LANGUAGE	BASIC	BASIC	BASIC
Priority Interupt	not available	15 levels	15 levels
Error Control	not available	standard	standard
VDU: Graphics	standard:semigraphics	optional:alphanumeric	standard:full graphics
Data Storage	flexible drive	cassette	cassette
Speed of Operation	adequate	good	excellent
b)			
Interfacing	IEEE	IEEE(optional) Bit Parallel(optional) Bit Serial (optional) BCD (optional)	IEEE BCD Bit Parallel Bit Serial Buffered I/O
c)			
Storage Capacity	32k	ca 50k	187k
Approx. Cost	5,000	16,500	32,000

a good calculator offers for the efficient running of an active research laboratory. A possible solution (although not an essential of the described system) would be the purchase of two calculators. The first, a sophisticated and probably more expensive calculator would be used to control the operation, the second cheaper calculator which in turn carries on the measurements. In this way the control calculator would be free to be used for the myriad of other uses one could envisage in a modern laboratory.

To summarise, the essential or basic properties of the computing portion can be satisfied by a cheaper calculator such as the PET 4032 calculator. However, on the grouds of predicted lifetime, programming characteristics and flexibility, considerable justification can be given for the purchase of a more sophisticated calculator. Although cost is a major consideration, the purchase of a calculator from the Hewlett Packard range gives an excellent possibility of on-going development of a computer controlled, highly flexible system.

Impedance Measurement Circuit

The basic circuit (Figure 2) for the measurement of the a.c. impedance consists of a waveform generator and analyser which are interfaced to the measurement cell by an impedance converter. (See Appendix I for the method of calculating the impedance with this circuit). A large number of instruments including Frequency Response Analysers, Network Analysers, Gain Phase Meters and Phase Sensitive Detectors are commercially available. Although the essential requirements listed in Table 2 together with the recommendation of IEEE (or similar) interfacing capability restricts this choice considerably, it is not possible to discuss all the options available and only three examples (Table 3) will be discussed.

The first, low cost system consists of a Hewlett Packard Function Generator and Gain Phase Meter. Although these two instruments meet all of the essential requirements listed in Table 2, two types of interfacing (IEEE and BCD, with model 3575A option 001) are required resulting in the necessity for a more sophisticated calculator or the building of special interfaces. Thus the type of system has been demonstrated successfully using custom built interface at Queen's University. Although noise rejection by this system is good, no signal averaging is available to improve performance under noisy conditions. The second, high cost system is IEEE compatible but offers little other advantage over the first example to justify the extra cost.

The third example, a Solatron 1174 Frequency Response Analyser, is probably the best impedance measurement equipment on the market today. (Note: for IEEE compatibility, it is necessary to purchase the Solartron 1183C interface.) It consists of a high stability generator combined with a high quality analyser in the same instrument. This has the advantage that correlation of the input and output signals can be used to reduce noise. Moreover the analyser used digital (averaging) techniques to perform precision measurements even in the presence of interfacer noise and harmonics. The level of averaging is programmable which allows the speed of operation to be greatly increased when noise is not a problem. Its low frequency (10^{-4} Hz) capability allows a much greater flexibility in the processes studied. For instance, electrode/electrolyte interface processes commonly occur in the frequency range from 10Hz to 0.01Hz, a range not covered by the other instruments discussed here.

In the field of ionic conductors, a wide range of conductivity values are encountered and it is necessary to have an analyser with a

TABLE 2

CHARACTERISTICS OF THE MEASUREMENT INSTRUMENTS

	ESSENTIAL	DESIRABLE
Maximum Frequency	500 kHz	1 MHz
Minimum Frequency	50 Hz	0.01 Hz
Externally controllable frequency range	3 decades	full range
Amplitude (minimum)	-	10 mV pk-to-pk
Input Impedance	1 MΩ	---

TABLE 3

EXAMPLES OF SUITABLE MEASUREMENT EQUIPMENT

	HP 3325A Function Generator HP 3575A Gain Phase Meter	HP 3040A Network Analyser (2 instruments)	Solartron 1174 F.R.A.
Frequency Range	1 Hz - 1 MHz	50 Hz - 13 MHz	10^{-4}Hz - 1 MHz
Amplitude	1 mV - 10 V	1 μV - 1 V	10 mV - 10 V
Interfacing Required	IEEE and BCD	IEEE	IEEE(optional)
Input Impedance	1 MΩ	1 MΩ	1 MΩ
Cost	9,000	19,000	27,500

high input impedance. All commercially available instruments have an input impedance of 1MΩ, and it is therefore necessary to include an impedance converter in the measurement circuit (Figure 2). In this figure, two balanced voltage followers are used to carry out this conversion and then can be custom built. The only commercially available method of performing this conversion is by the use of the Solartron Electrochemical Interface (Model 1186). This is an extremely powerful instrument as it not only performs the impedance conversion but also acts as a high precision potentiostat and galvanostat, instruments which are essential in an electrochemical laboratory. It has been designed to operate with the Solatron 1174 Frequency Response Analyser.

Temperature Measurement and Control

For many applications, it is necessary to know the temperature dependence of the conductivity and it is highly desirable to have this measurement under computer control (measurements can then be measured overnight freeing the instruments during the working day for analysis etc.) However there seem to be no IEEE compatible temperature controllers on the market and it is necessary to build a special interface for this purpose. The only requirements are that the instrument have a remote control option and be compatible with the chosen temperature range (usually room temperature to 1000°C). Many instruments such as the ThermoElectric Spectrol 800 meet these requirements and no firm recommendation can be given. Temperature measurement can be simply carried out with an IEEE compatible digital multimeter at a relatively low cost.

Summary

The above discussion has led to the choice of three possible systems which are summarised in Table 4. The cheapest system (1) employs a PET Calculator as the control instrument with a Solartron Frequency Response Analyser as the measurement instrument. As the calculator has only IEEE interfacing capability, this system relies on IEEE compatibility. Although having highly sophisticated measurement circuitry, the choice of calculator results in the disadvantages of limited software possiblities and poor data handling capabilities. The choice of a more sophisticated calculator, the HP System 45 allows the choice of cheaper impedance measurement instruments using BCD interfacing (system 2). Although this has the advantage of single manufacturer compatibility, the measurement flexibility is reduced. Combination of the high software quality of the HP Calculator and the high accuracy of the Solatron Frequency Response Analyser produces a system which must rank as a world leader in the market today. It is this system which must be most highly recommended.

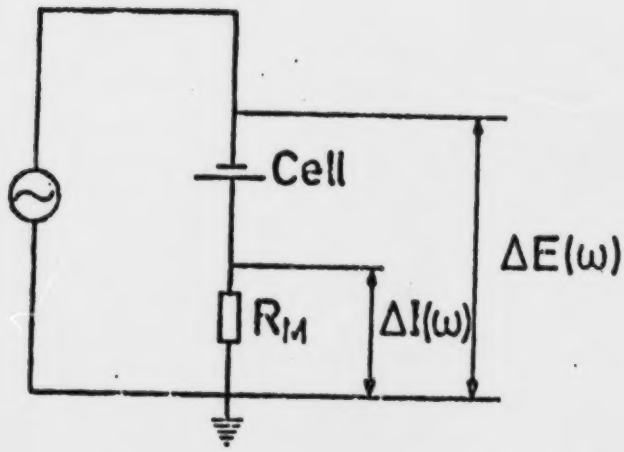
TABLE 4

POSSIBLE SYSTEMS AND THEIR APPROXIMATE COST

Calculator	PET 4032	HP 9800 System 45	HP 9800 System 45
Peripherals	PET Tractor Printer	-	-
	PET Flexible Disc Drive	-	-
Impedance Measurement	Solatron 1174 F.R.A.	HP 3325A + HP 3575A	Solatron 1174 F.R.A.
Temperature Controller	(Arbitrary)*	(Arbitrary)*	(Arbitrary)*
Temperature Measurement	IEEE Compatible DMM*	IEEE Compatible DMM*	IEEE Compatible DMM*
Approx. Total Cost	35,000*	45,000*	60,000*
Optional Extra	Solartron Electrochemical Interface ($6,000)	-	Solatron Electrochemical Interface ($6,000)

* As a large number of commercially available instruments meet these requirements, no firm recommendation is given. However allowance has been made for these items in the approximate total cost.

APPENDIX I



$$Z_{CELL}(\omega) = \frac{\Delta E(\omega)}{\Delta I(\omega)} - R_M$$

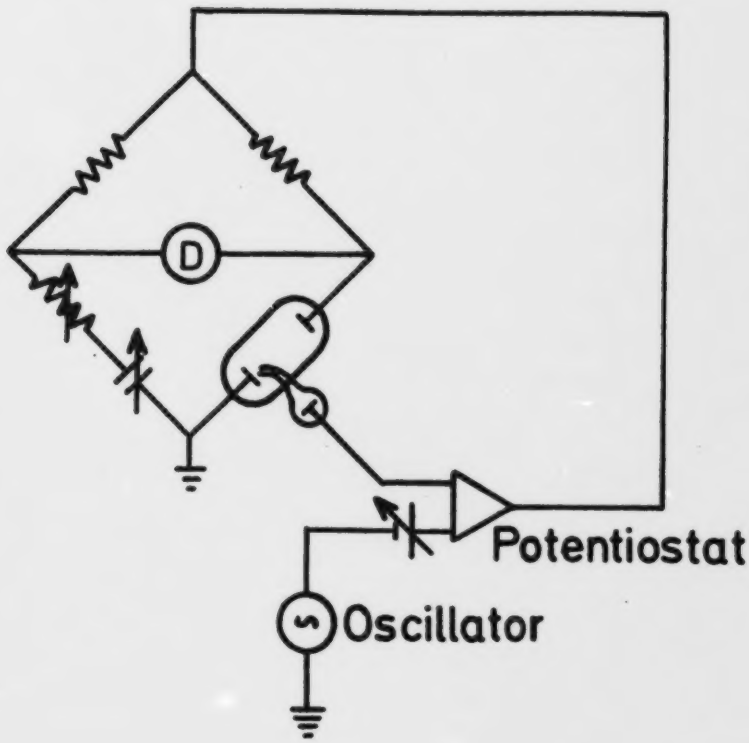


FIG 1

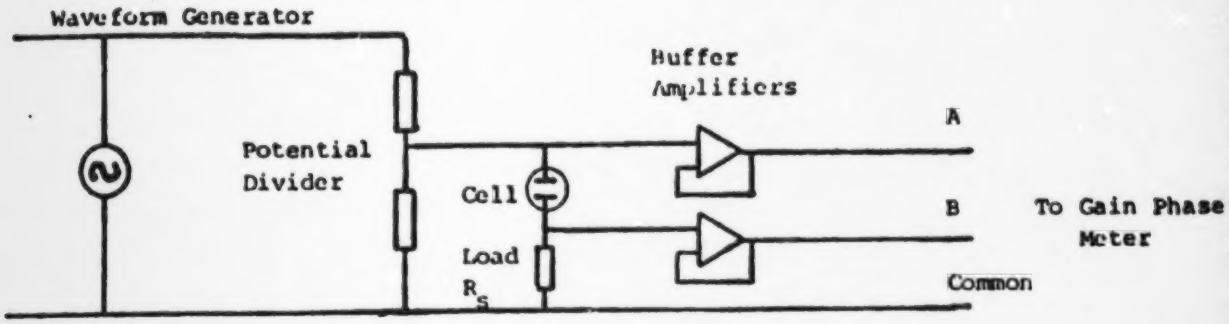


Fig. 2 Measurement Circuit